PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

MUNEKATA ET AL

Application No.: 10/666,129 Art Unit: 1742

Filed: September 22, 2003 Examiner: Sikyin Ip

For: LEAD-FREE SOLDER ALLOY

DECLARATION UNDER 37 CFR 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Further to my declaration of March 17, 2005, I, Yoshitaka Toyoda, declare as follows:

I am one of the joint inventors of this patent application. My background is described in the declaration of March 17, 2005.

In order to demonstrate the effects of the Cu content on a Sn-Cu-Ni-P solder alloy, I

performed a wettability test on the solder alloys listed in attached Table 1 ("Wetting time of Sn-Cu-Ni-P alloys"). Wettability was measured by the meniscograph method set forth in JIS 3910. The meniscograph method is described in paragraph 12 of the declaration of March 17, 2005. Attached Figure 1 ("Wetting balance method") illustrates the steps in the method. The "wetting time" shown in Table 1 is the zero crossing time for each alloy. The lower the zero crossing time, the better is the wettability of a solder.

The values in Table 1 are graphed in attached Figure 2 ("Wetting time of Sn0.05Ni0.003P + Cu alloys"). In this figure, the solid line is a least squares curve for the wetting time when Cu = 0%, 2.0%, and 2.5%. The dashed line connects all the measured values.

Table 1 and Figure 2 show that when Cu is added to a Sn-Ni-P alloy, the wettability of the alloy increases (the wetting time decreases) as the Cu content increases and is best at a Cu content of around 0.7 mass %. Wettability then begins to decrease (the wetting time increases).

Figure 2 shows that there is a marked drop in the zero crossing time and a marked improvement in wettability when Cu is in the range of 0.1 to 1.5 mass % compared to when Cu is outside this range. Therefore, a Cu content of 0.1 to 1.5 mass % produces an unexpected effect.

The values in Figure 2 are for an alloy containing 0.05% Ni and 0.003% P. If Ni or P is changed from these values, the whole curve in the graph may move up or down but the trend will

be the same.

To illustrate the effect of the liquidus temperature of a Sn-(Cu)-Ni-P alloy on the quality of solder joints formed by flow soldering, I performed a test of actual flow soldering on the alloys shown in Table 1. Attached Fig. 3 ("Method of testing for bridging and non-wetting") illustrates the test method. The pins of 8-pin connectors (having a pitch of 2.5 mm between pins) were inserted into holes in a paper-phenol substrate. The pins were then dipped into molten solder at 255 deg. C for 5 sec as shown in Fig. 3. The substrate was lifted out of the molten solder and the condition of the solder joints formed on the pins on the bottom of the substrate was observed. I evaluated the joints for bridging and non-wetting.

Attached Fig. 4 ("Evaluation of joint quality") shows examples of good and bad solder joints. A good joint had no bridging between joints. A joint with a bridging between joints was evaluated as no good (NG). A joint with a non-wetting portions where a copper land on the substrate was visible was also evaluated as no good (NG). I counted the number of bridging and non-wetting portions on each substrate.

The results of evaluation are shown in attached Table 2 ("Bridging and non-wetting by Sn-Cu-Ni-P Alloys"). From the standpoint of bridging portions and non-wetting portions, satisfactory results were obtained when Cu = 0 to 1.5%. The results were not satisfactory when Cu = 2.0% and above.

For alloy no. 7 which had a liquidus temperature of 412 deg. C, I also observed needle-shaped intermetallic compounds (IMC) that projected from some joints. Attached Fig. 5 ("Needle-shaped intermetallic compounds") shows examples of needle-shaped IMC. A needle-shaped IMC is undesirable because it can cause a short circuit between joints.

Attached Fig. 6 ("Incidence of bridging vs liquidus temperature") is a graph showing the occurrence of bridging in Table 2 as a function of liquidus temperature. Attached Fig. 7 ("Incidence of non-wetting vs liquidus temperature") is a graph showing the occurrence of non-wetting portions in Table 2 as a function of liquidus temperature.

Fig. 6 and Fig. 7 show that in order to obtain acceptable joints, it is desirable for the liquidus temperature of a solder alloy to be 300 degree C or less.

Attached Figure 8 ("Relationship between Cu and Ni content") shows the relationship between the Cu content and the Ni content in a Sn-Cu-Ni-P alloy when the liquidus temperature of the alloy is 300 deg. C. At points on the line in the graph, the liquidus temperature of the alloy = 300 deg. C. At points below the line in the graph, the liquidus temperature is less than 300 deg. C. At points above the line in the graph, the liquidus temperature is greater than 300 deg. C. The P content does not affect the liquidus temperature. From this figure, it can be seen that for all values of Cu in the range of 0.1 to 1.5%, it is possible to select a value of Ni which is at most 0.3% for which the liquidus temperature is at most 300 deg. C.

I measured the liquidus temperatures of various Sn-Cu-Ni-P alloys to determine the effect of the Cu content and the Ni content on the liquidus temperature. The measurements are shown in attached Fig. 9 ("Liquidus temperature of Sn-Cu-Ni-P alloys"). The P content for each alloy was a constant value of 0.003 % because P does not affect the liquidus temperature.

Fig. 9 shows that when the Ni content is 0.3%, it is possible to obtain an alloy having a liquidus temperature of 300 deg. C or less with various Cu contents. In contrast, when the Ni content is 0.5 % or greater, the lowest liquidus temperature for a Sn-Cu-Ni-P alloy is 350 deg. C when Cu = 0 % and is higher when Cu is greater than 0 %. This means that a Sn-Cu-Ni-P alloy in which Ni is 0.5% or above cannot be effectively used for soldering of electronic parts because it will produce defects like those shown in Fig. 4 and Fig. 5.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Yoshitaka Toyoda — Oct. 13, 2007

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Date

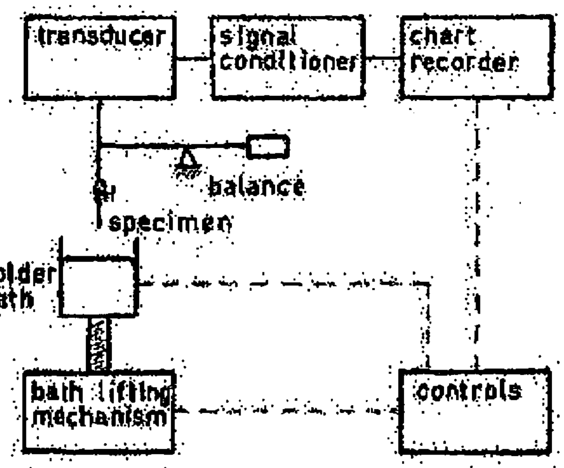


Fig. 7.3 Block diagram of wetting balance.

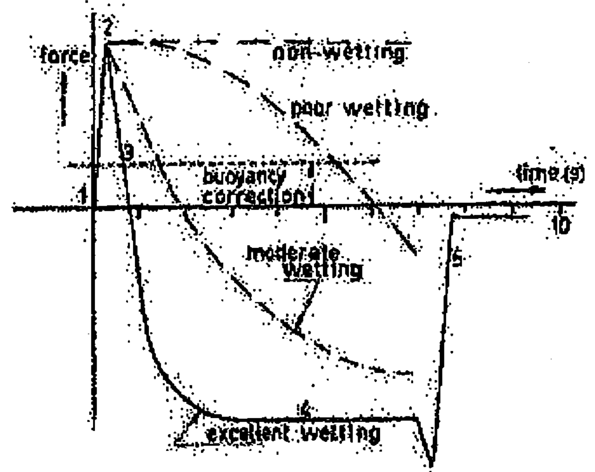
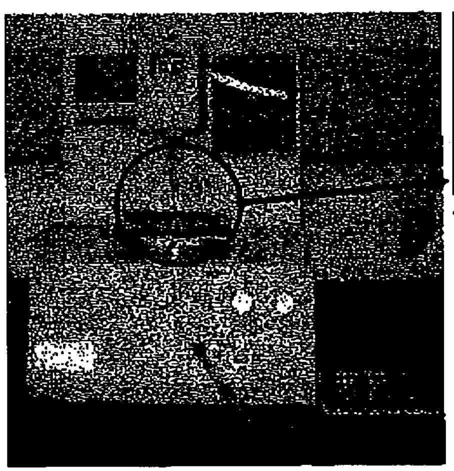
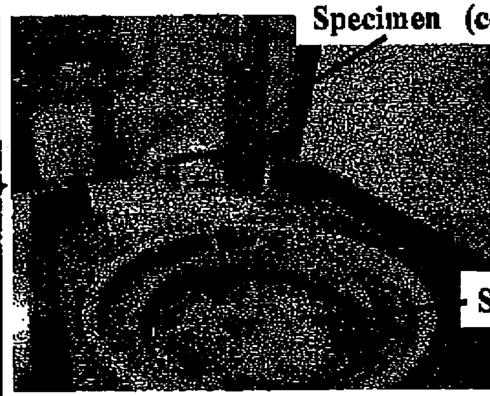


Fig. 7.5 Recorder traces of forces exerted on a specimen during the test period in a wetting balance. The figures beside the solid curve correspond to the situations shown in Fig. 7.4.





Specimen (copper plate)

Solder

Test equipment (Made of Resca Ltd.)

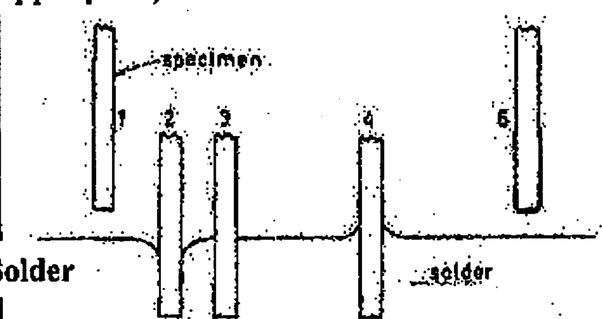
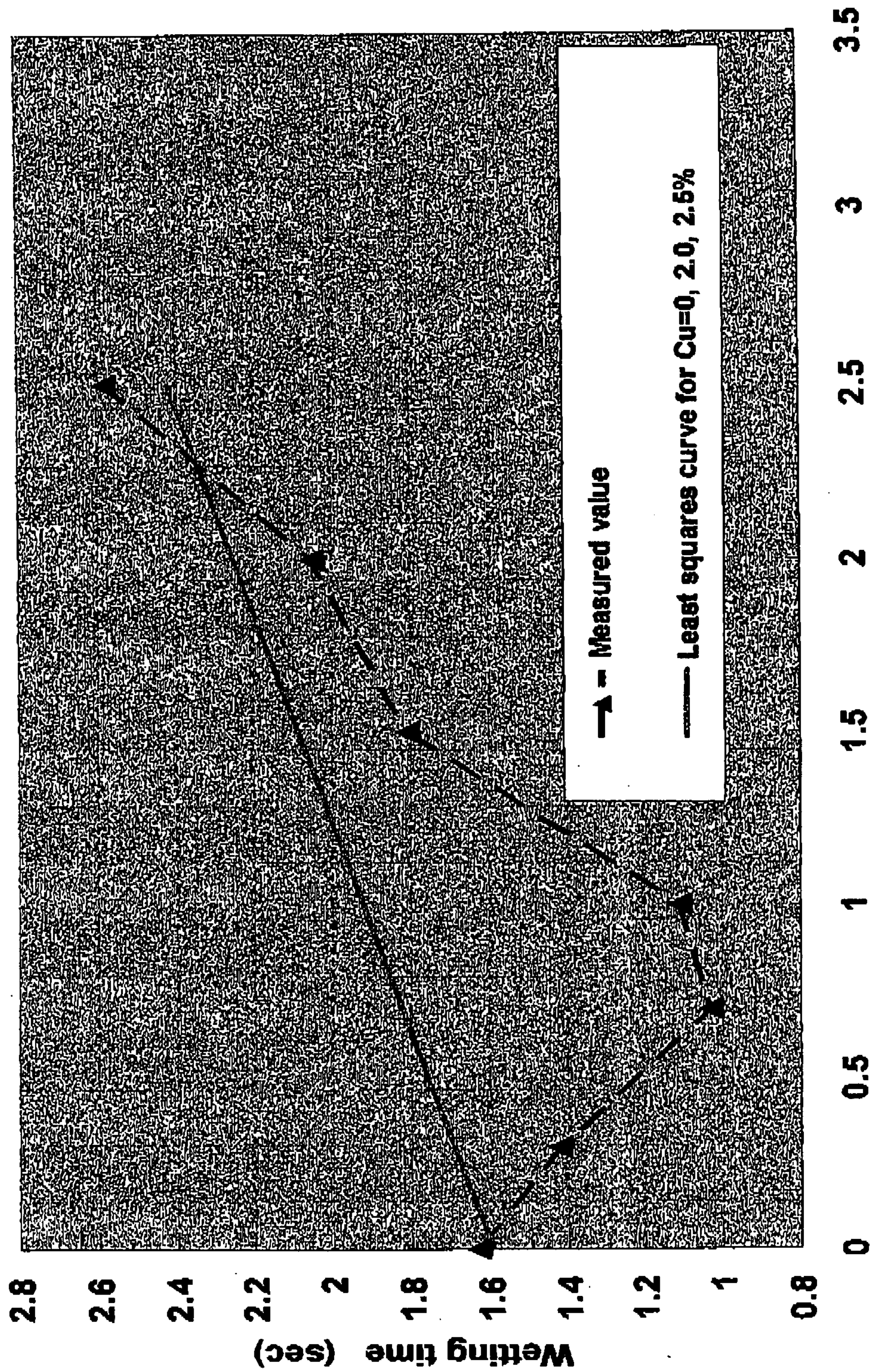


Fig. 7.4 Five positions of a readily wettable specimen in a wetting balance (see text).

Fig.1 Wetting balance method

[Reference: Soldering in Electronics (1984 by Wassink)]

Fig.2 Wetting time of Sn0.05Ni0.003P+Cu alloys



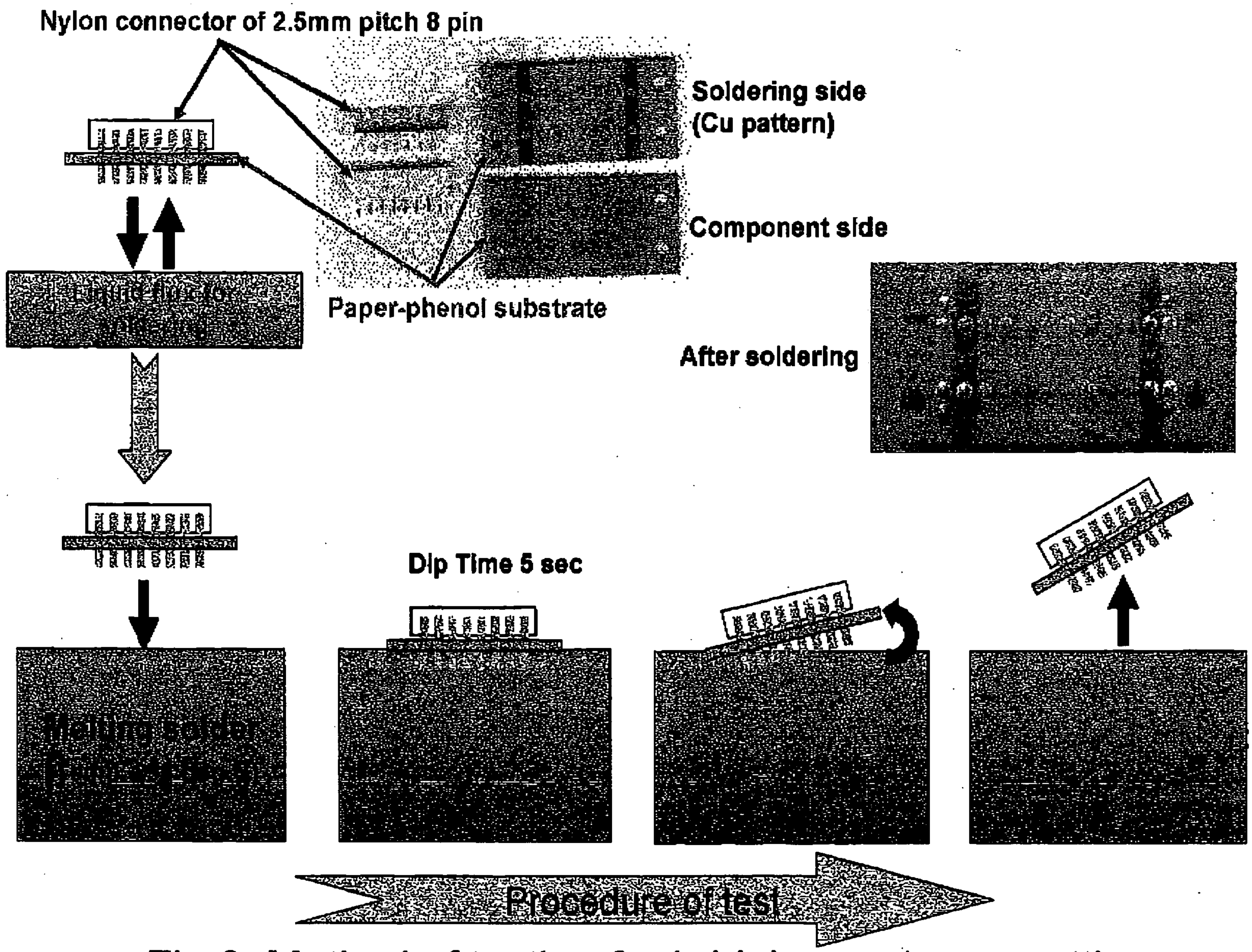


Fig.3 Method of testing for bridging and non-wetting

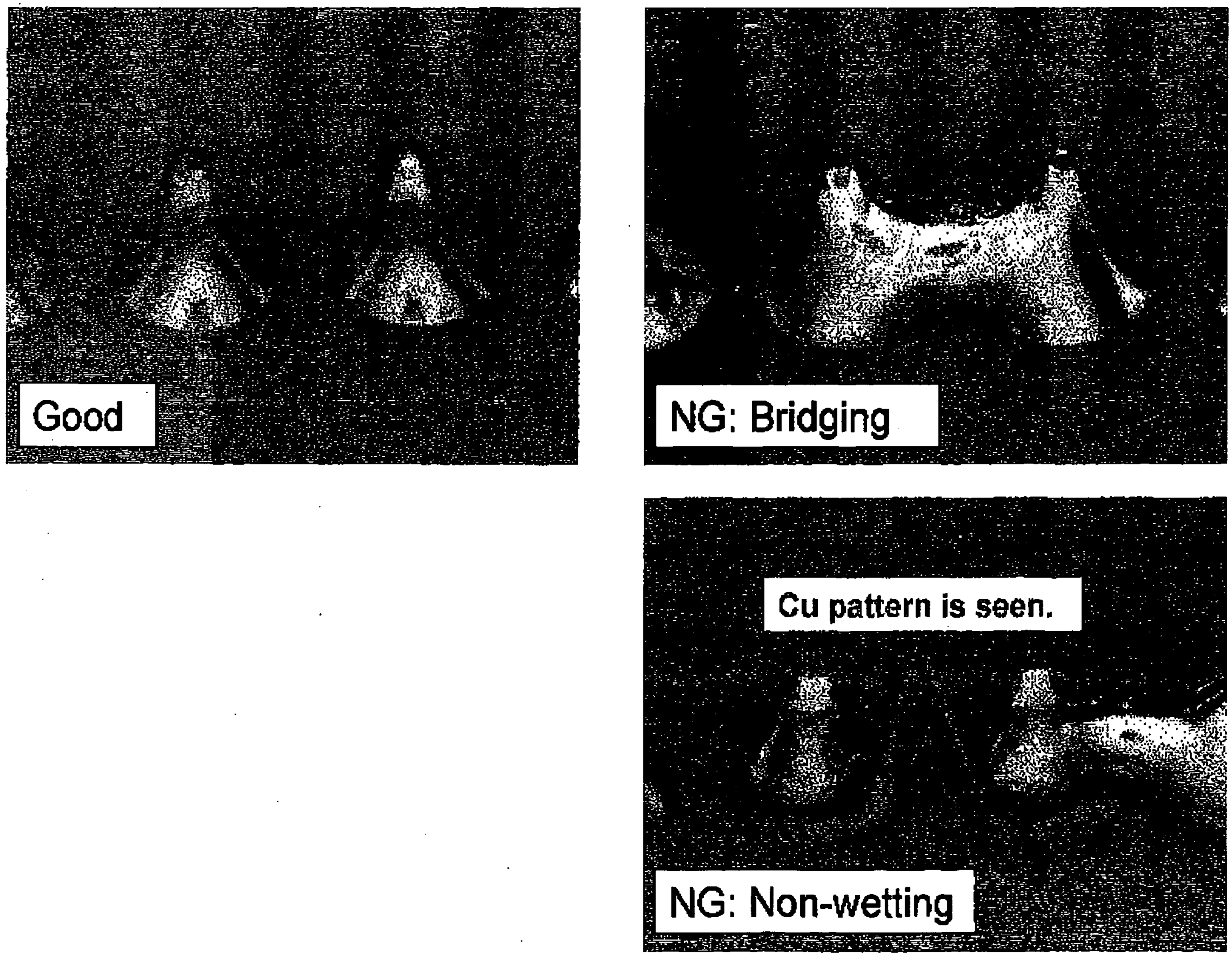


Fig.4 Evaluation of joint quality

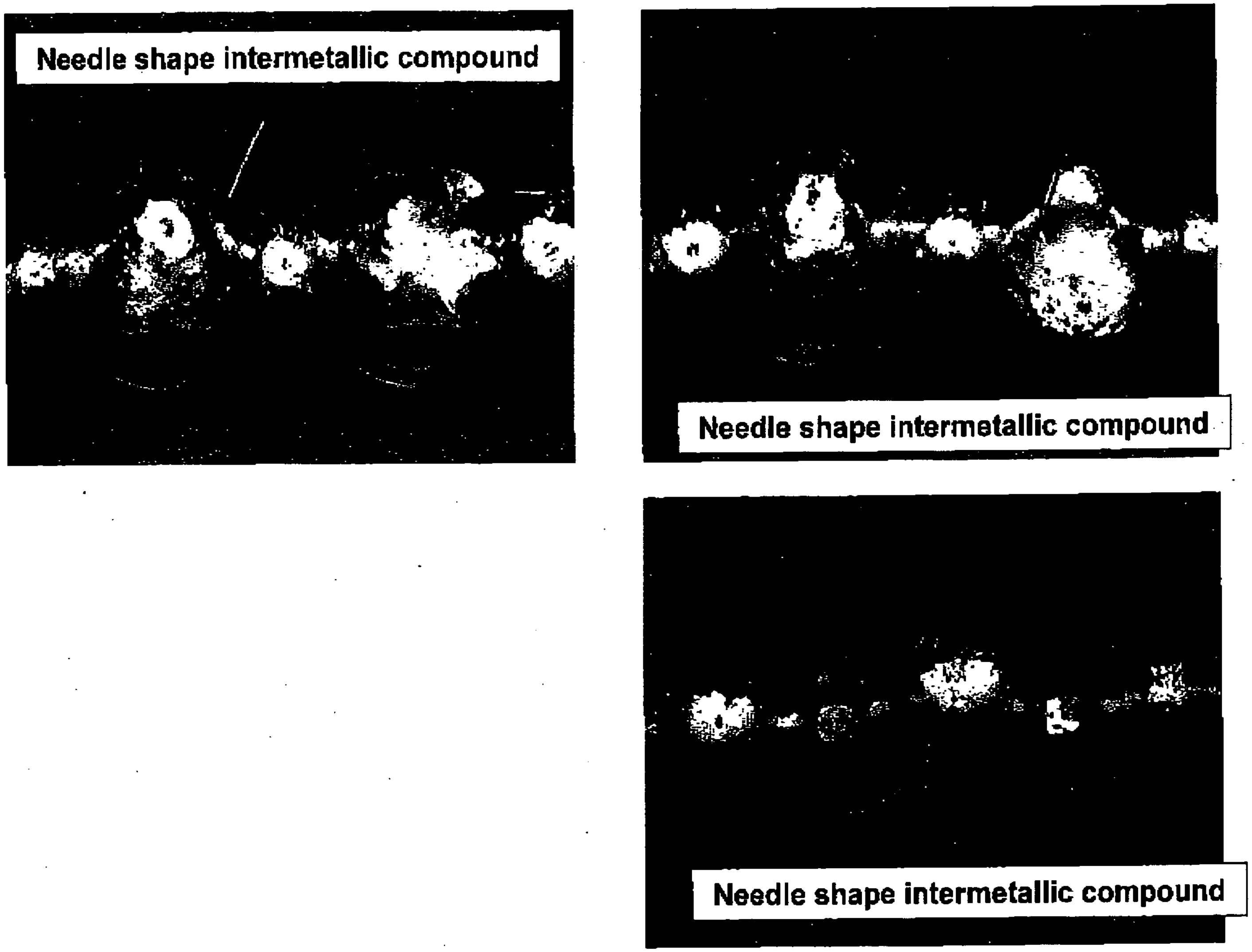


Fig.5 Needle-shaped intermetallic compounds

Fig.6 Incidence of bridging vs liquidus temperature

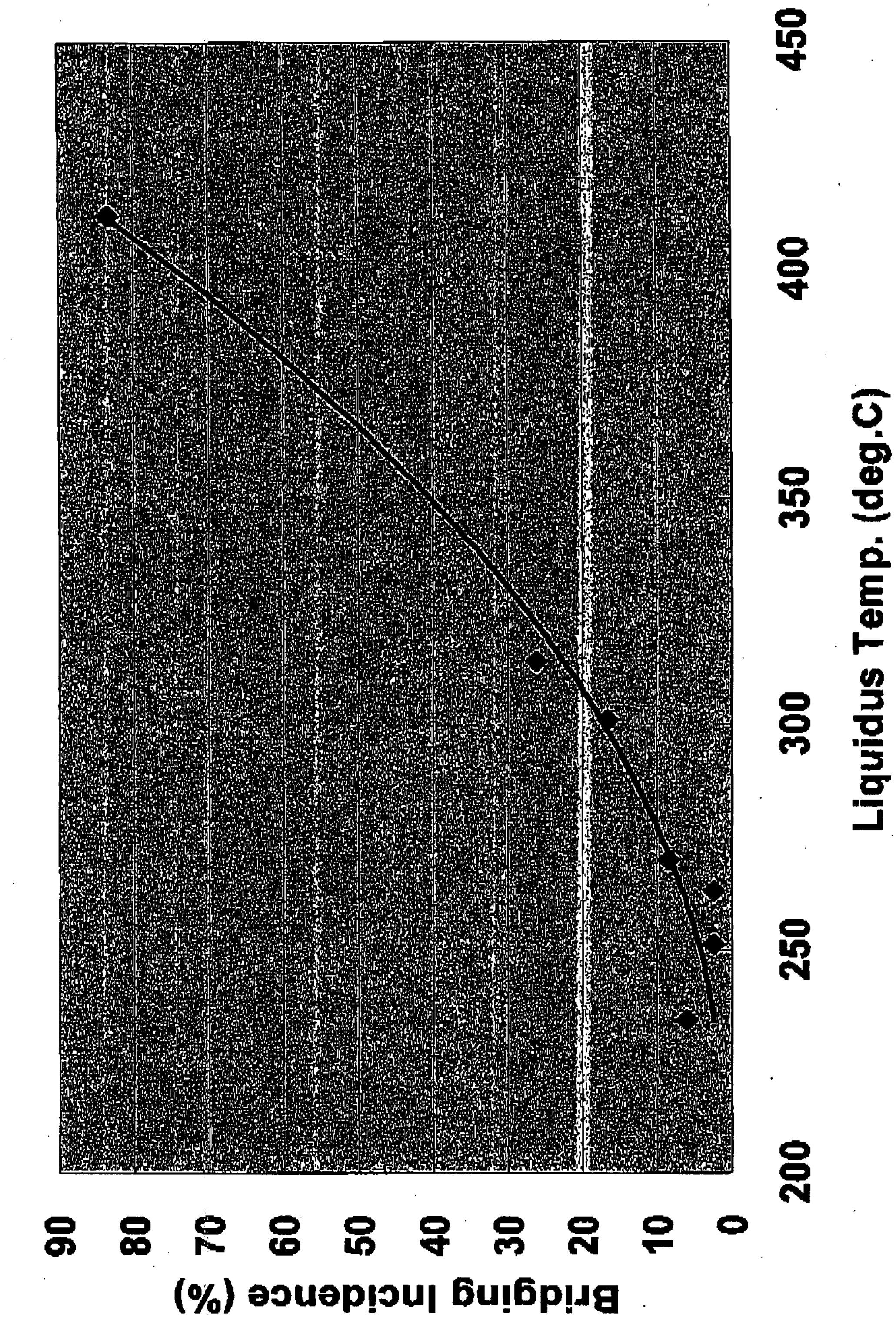


Fig.7 Incidence of non-wetting vs liquidus temperature

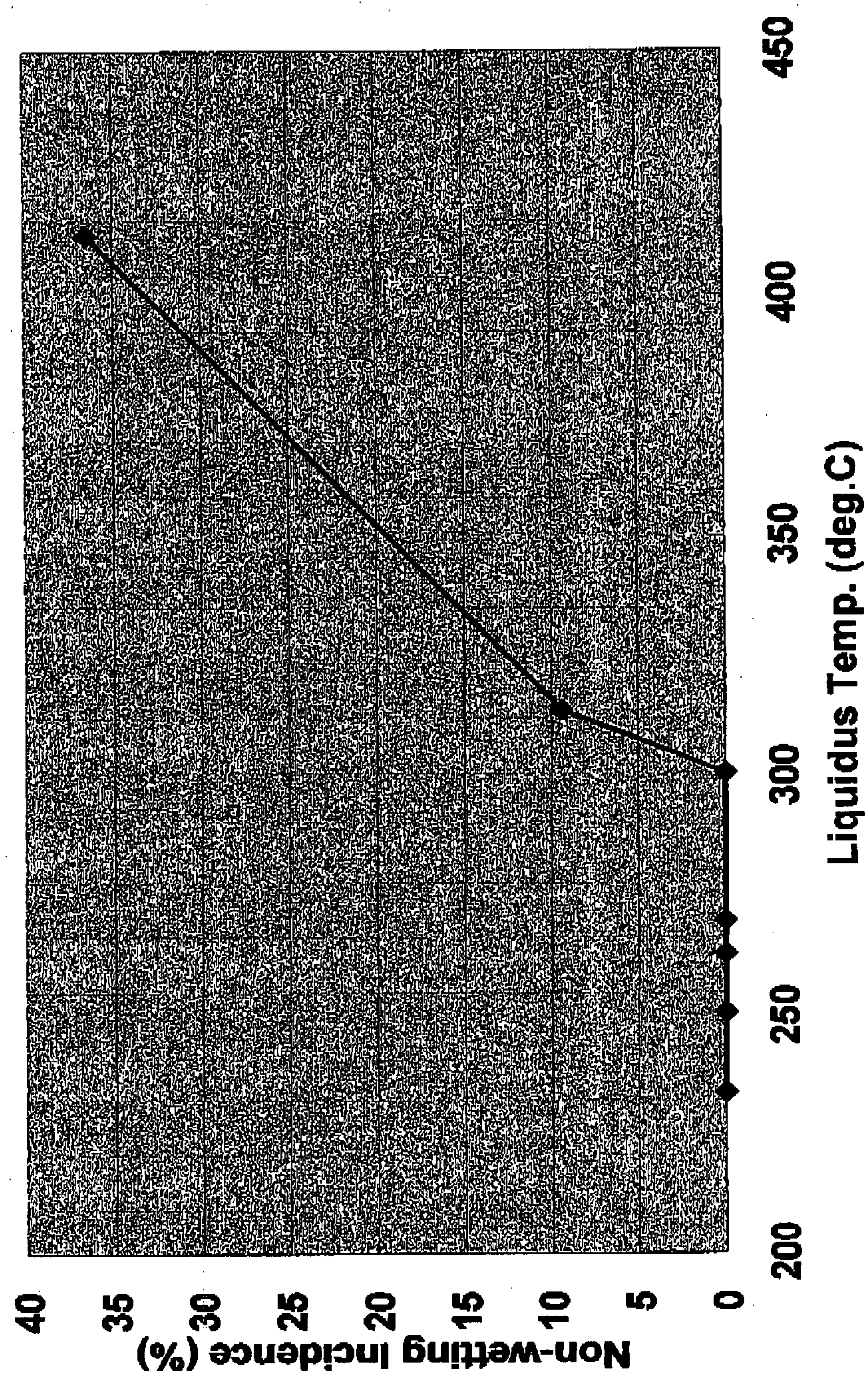


Fig.8 Relationship between Cu and Ni content
(For liquidus temperature 300 deg.C)

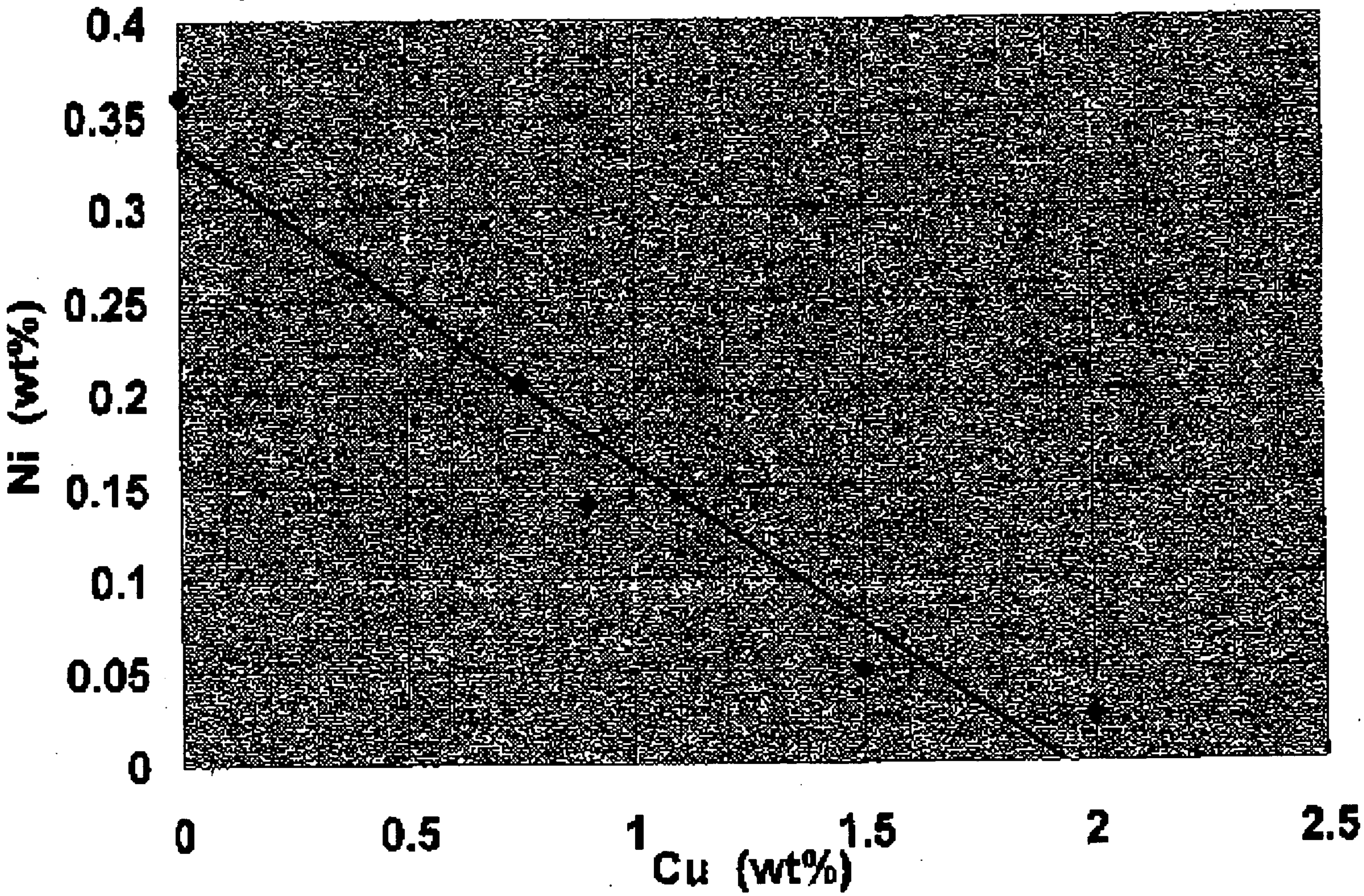


Fig.9 Liquidus temperature of Sn-Cu-Ni-P alloys

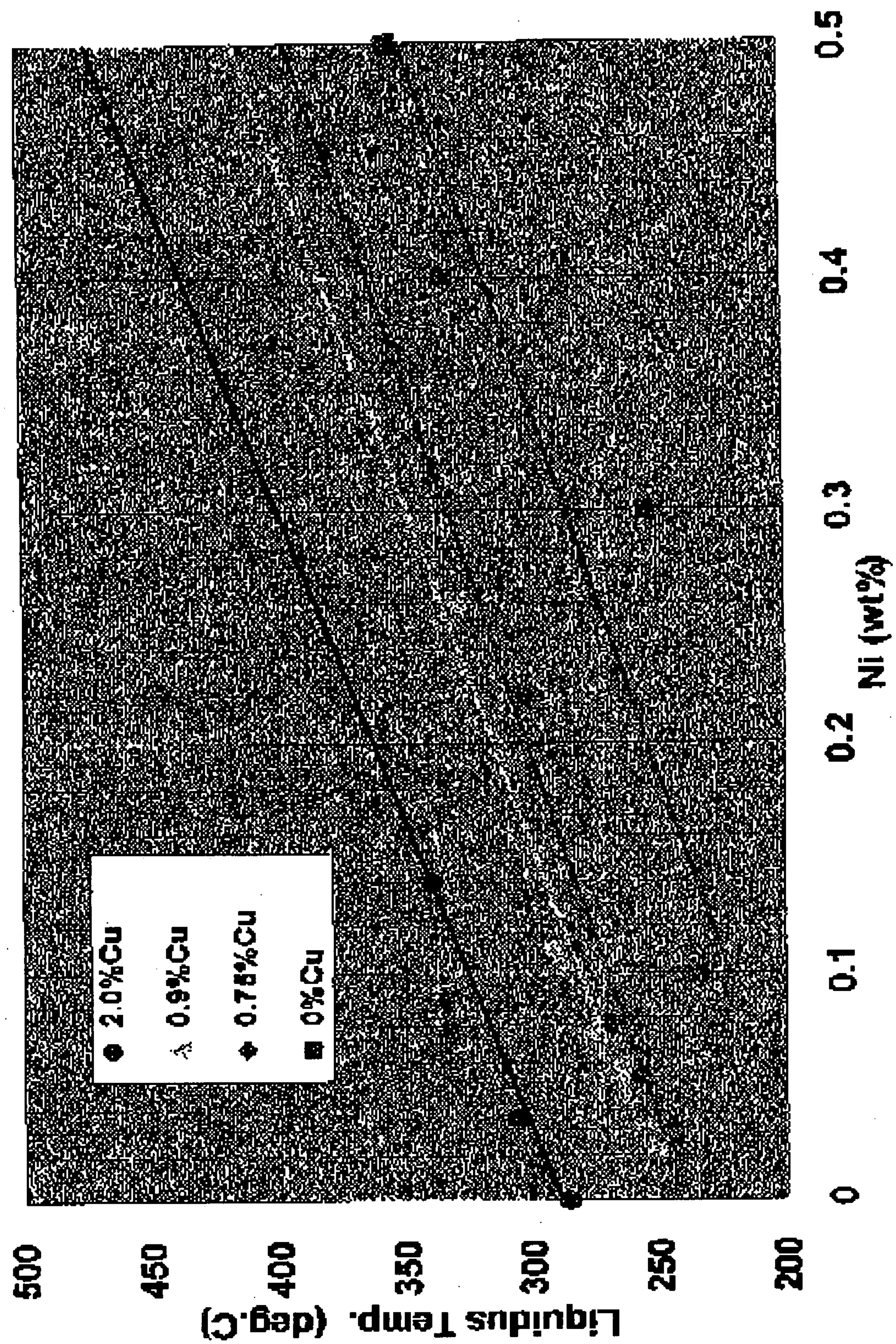


Table 1 Wetting time of Sn-Cu-Ni-P alloys

No	Solder Composition	Wetting Time (sec)
1	Sn-0.05Ni-0.003P	1.63
2	Sn-0.3Cu-0.05Ni-0.003P	1.42
3	Sn-0.7Cu-0.05Ni-0.003P	1.03
4	Sn-1Cu-0.05Ni-0.003P	1.11
5	Sn-1.5Cu-0.05Ni-0.003P	1.81
6	Sn-2.0Cu-0.05Ni-0.003P	2.05
7	Sn-2.5Cu-0.05Ni-0.003P	2.56

Table 2 Bridging and non-wetting by Sn-Cu-Ni-P alloys

No	Solder Composition	Melting Temperature (deg.C)	Bridging (n=84)		Non-wetting (n=96)	
		Solidus - Liquidus	Number	Incidence(%)	Number	Incidence(%)
1	Sn-0.05Ni-0.003P	232-234	5	6.0	0	0.0
2	Sn-0.3Cu-0.05Ni-0.003P	228-263	2	2.4	0	0.0
3	Sn-0.7Cu-0.05Ni-0.003P	227-261	2	2.4	0	0.0
4	Sn-1Cu-0.05Ni-0.003P	228-270	7	8.3	0	0.0
5	Sn-1.5Cu-0.05Ni-0.003P	227-301	14	16.7	0	0.0
6	Sn-2.0Cu-0.05Ni-0.003P	228-314	22	26.2	9	9.4
7	Sn-2.5Cu-0.05Ni-0.003P	227-412	70	83.3	35	36.5